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ATTACHMENT 1

**SURFICIAL SOIL SAMPLING PLAN
OF THE
FINAL PHASE II RCRA FACILITY INVESTIGATION
REMEDIAL INVESTIGATION
WORK PLAN (ALLUVIAL)**

REVISION 1

**ROCKY FLATS PLANT
903 PAD MOUND AND EAST TRENCHES AREAS
(OPERABLE UNIT NO 2)**

ENVIRONMENTAL RESTORATION PROGRAM

**U S Department of Energy
Rocky Flats Office
Golden Colorado**

5 February 1991

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REVIEWED FOR CLASSIFICATION/UCN	
BY	G T Ostdek <i>GT</i>
DATE	<i>2-12-93</i>

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ATTACHMENT 1 SURFICIAL SOIL SAMPLING PLAN

TABLE OF CONTENTS

<u>SECTION</u>	<u>TITLE</u>	<u>PAGE</u>
1 1	Statement of the Problem	1-1
1 2	Objectives	1-1
1 3	Spatial Distribution of Plutonium and Americium East of Rocky Flats Plant	1-2
1 3 1	Geostatistical Kriging Approach	1-2
1 3 2	Source of Kriging Variations in Soil-Plutonium Concentrations in Surface Soils	1-7
1 3 3	Ground Based Gamma Study	1-9
1 3 4	Proposed Work	1-9
1 4	Vertical Distribution of Plutonium and Americium in Soils East of Rocky Flats Plant	1-15
1 4 1	Past Work	1-15
1 4 2	Proposed Work	1-16
1 5	Physiochemical Association of Plutonium in Rocky Flats Plant Soils	1-18
1 5 1	Static Soil Phase - Past Work	1-18
1 5 2	Static Soil Phase - Sequential Extraction Experiments	1-19
1 5 3	Static Soil Phase - Proposed Work	1-20
1 5 3 1	Tracer Study	1-20
1 5 3 2	Partitioning of Soil Phases	1-22
1 5 3 3	Experimental Conditions	1-23
1 5 4	Mobil Soil Phase - Past Work	1-24
1 5 5	Mobil Soil Phase - Proposed Work	1-25
1 5 5 1	Soil Solution Samplers	1-26
1 5 5 2	Precipitation Events Simulation	1-30

LIST OF TABLES

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE</u>
1-1	Soil-Plutonium Concentrations in Surface Soils East of 903 Pad	1-8
1-2	Soil Types East of 903 Pad	1-17

ATTACHMENT 1
SURFICIAL SOIL SAMPLING PLAN
TABLE OF CONTENTS (Continued)

LIST OF FIGURES

<u>FIGURE</u>	<u>TITLE</u>	<u>PAGE</u>
1-1	Kriging Estimates for Plutonium in Soils Based on 1975-1978 Studies	1-4
1-2	Isotropic Semivariogram	1-5
1-3	Kriging Standard Deviation for Plutonium in Soils Based on 1975-1978 Studies	1-6
1-4	Kriging Estimates for Americium in Soils Based on 1990 Studies	1-10
1-5	Kriging Standard Deviation for Americium in Soils Based on 1990 Studies	1-11
1-6	Kriging Estimates for Plutonium in Soils Based on 1990 Studies	1-12
1-7	Kriging Standard Deviation for Plutonium in Soils Based on 1990 Studies	1-13
1-8	Proposed Surficial Soil Sampling Locations	1-14
1-9	Sequential Extraction for Soil-Pu	1-21
1-10	Soil Solution Sampler Apparatus	1-27
1-11	Schematic Diagram of TDR Soil Moisture Probes	1-29

ATTACHMENT 1
SURFICIAL SOIL SAMPLING PLAN

1 1 STATEMENT OF THE PROBLEM

The contamination of soils around Rocky Flats Plant by Plutonium (Pu) oxides was mainly caused by leaking barrels of Pu-contaminated oil in the area known as 903 Pad (Krey and Hardy, 1970). Numerous studies (Krey and Hardy, 1970, Seed et al, 1971, Poet and Martell, 1972, Johnson et al, 1976, Little, 1980, Little et al, 1980) concluded that surficial soils in the area east of 903 Pad are contaminated with Pu and Americium (Am) due to wind dispersal of soil particles during cleanup operations. More recently, Phase I RI of the OU No. 2 (Rockwell International, 1987a) found that the concentrations of Pu and Am were elevated in composite soil samples adjacent to Trench T-2 (BH25-87, BH 26-87, and BH27-87) and the Reactive Metal Destruction Site (BH28-87) T-1 (boreholes BH35-87 and BH36-87). In addition, the Phase I RI found occasional elevated concentrations of Pu (> 0.05 pCi/l) in filtered surface water samples from seeps (SW-50, SW-53, and SW-54) and in stream sediments (> 0.9 pCi/g) along Woman Creek (SED-25, SED-26, SED-29, and SED-30). It has been suggested that the source of the contaminated sediments were the surface soils from the 903 Pad area which were transported by wind. However, the elevated concentrations of Pu in seep waters above Woman Creek suggest that some of the Pu may travel in surface and ground water. Also, soil sampling results indicate that the actinides are enriched near the soil surface. Further investigation is necessary to characterize the transport mechanisms that control the spatial and vertical distribution of these radionuclides.

1 2 OBJECTIVES

The objectives of the proposed work plan for the surficial soils are to determine the spatial and vertical extent of Pu and Am in soils of the remedial investigation areas and in the buffer zone, study the physicochemical association of Pu and Am in soils (static and mobile soil phases) above seeps SW-50, SW-53, and SW-54, study the movement of both water and radionuclides (colloidal and dissolved) down the soil

column, and ascertain the hydrogeochemical relationships between the soil interstitial water and the seeps downslope

1 3 SPATIAL DISTRIBUTION OF PLUTONIUM AND AMERICIUM EAST OF ROCKY FLATS PLANT

1 3 1 Geostatistical Kriging Approach

The spatial dependency and distribution of actinides in soils will be studied through the use of geostatistical techniques. The key concept of geostatistics is the regionalized variable. The variable is a function describing the geographical distribution of an environmental contaminant such as Pu and Am in the soil environment. A principal concern of geostatistics is to relate the results obtained from one method to that obtained from another method (i.e., Rocky Flats Plant (RFP) vs. Colorado Department of Health (CDH) soil sampling techniques). These characteristics of geostatistics will therefore allow the use of historical data together with results generated by Phase II. For example, the spatial distribution of Pu and Am in the soils collected using the RFP method (data collected in 1971, 1975 to 1978, EG&G/EM aerial gamma surveys 1982 and 1990, and EG&G surface radiological survey 1990, and the annual soil sampling) will be compared against the spatial distribution of Pu and Am using the CDH methodology.

Kriging will be used to make spatial distribution (contour) maps. Unlike conventional contouring subroutines, kriging uses certain statistical optimal properties and provides measures of the error of the contoured surface. Kriging uses the information from the semivariogram to find an optimal set of weights that are used in the estimation of the surface at unsampled locations. The semivariogram describes the rate of change in a regionalized variable and measures the degree of spatial dependence between samples within geographical boundaries. The variogram splits the total variance in a data set into two parts. The first represents the spatial differences between the values of the samples taken at points separated by increasingly large distances, whereas the second represents local or short-range variances. The latter is called the nugget variance which represents random variance. Because the semivariogram is a function of distance, the weights change according to the geographical arrangement of the samples (Isaaks and Srivastava, 1989).

The need for better understanding of the spatial and vertical distribution of Pu were recognized many years ago by the Committee Evaluation of Pu Levels in Soils within and surrounding a U S Atomic Energy Commission (AEC) Installation at Rocky Flats, Colorado (Seed et al , 1971) They recommended that the mechanism of Pu transport in soil be addressed, and the chemical form of Pu in Rocky Flats Plant soils should be determined In response to these recommendations both extensive and intensive studies were conducted

The extensive study sites are located east of the 903 Pad (Figure 1-1) The concentrations of soil-Pu depicted in Figure 1-1 clearly suggest a spatial trend from west to east The strong west-east vector suggests that wind is the most probable force that controlled Pu transport across the landscape The variogram computation suggests a gaussian model with nugget of 0.34, sill of 0.71 and a range parameter of 1,237 (Figure 1-2) The gaussian model was computed using the following formula

$$\gamma(h) = C_0 + C[1 - \exp(-h^2/A_0^2)]$$

where

$\gamma(h)$ = variogram,

(h) = lag interval,

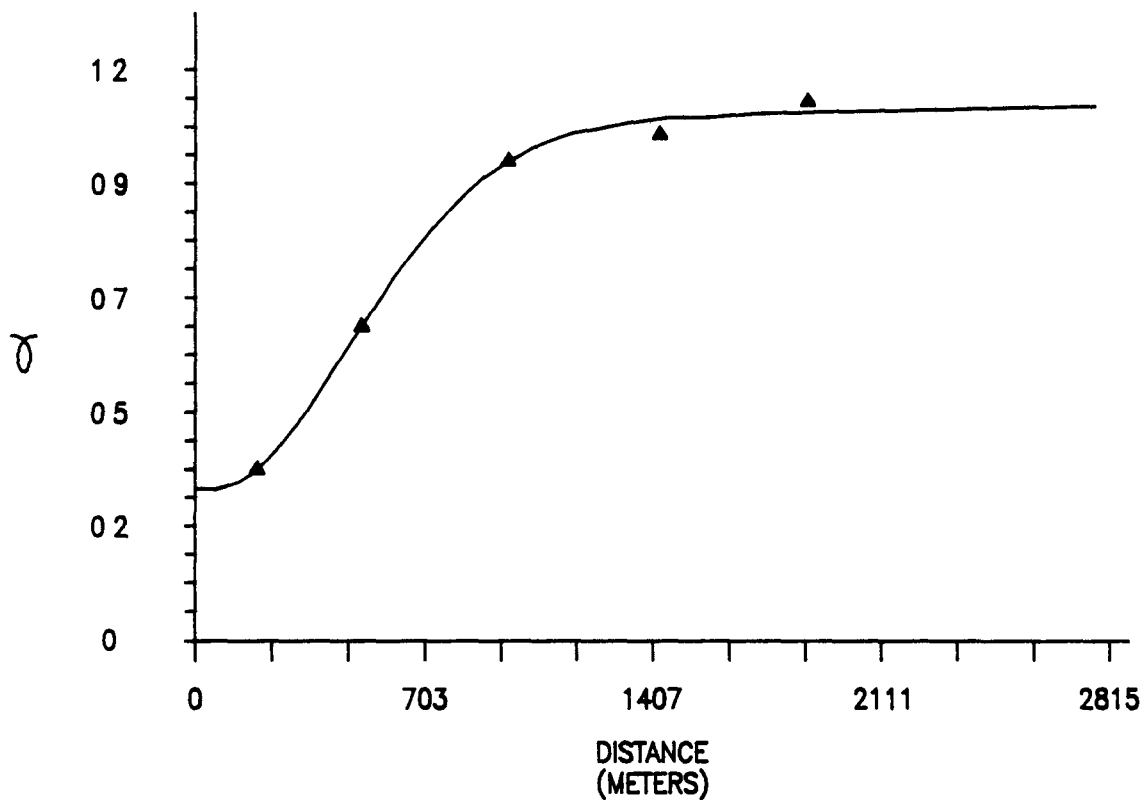
C_0 = nugget variance,

C = sill, and

A_0 = range parameter

Kriging estimates using the gaussian model were computed for the extensive study sites and are depicted in Figures 1-1 and 1-3 Figure 1-1 depicts contours of soil-Pu estimates in the buffer zone east of 903 Pad Kriging permits one to estimate the variance of each estimated mean and hence to assess whether additional data are needed in a given area The main sources of the error estimates are (1) number of the nearby samples, (2) proximity of the available samples, (3) spatial arrangement, and (4) the nature of the contaminant Figure 1-3 illustrates the kriging standard of error estimates which are low in the center of the buffer zone, and which verify the goodness-of-fit of the kriging estimates in this location However, large error estimates were observed near the 903 Pad and in the northeast and southwest corners of the grid (Figure 1-3)

ISOTROPIC SEMIVARIOGRAM GAUSSIAN MODEL



THE VARIOGRAM MEASURES THE DEGREE OF
CORRELATION AMONG Pu VALUES IN A GIVEN
AREA AS A FUNCTION OF DISTANCE AND
DIRECTION BETWEEN SAMPLES

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ISOTROPIC SEMIVARIOGRAM

FIGURE 1-2

February, 1991

These findings strongly suggest that larger data set is needed in order to better estimate the spatial distribution of Pu east of 903 Pad

The traditional method of mapping (hand-contouring or computer generated contour maps) usually produces smooth contours that honor the data at known points. This technique usually produces fairly erratic contours. Geostatistical techniques will produce a much smoother map that shows the general trend of a given pollutant (e.g., Figure 1-1). In addition, kriging will provide an estimate of the errors of estimation for the general trend (Figure 1-3) as well as the correlation between sample values at the sampling interval used. A cross section through the traditional map will show the up and down necessary to fit a smooth curve through the data, whereas the kriged section line will show a broad general trend and differs from the data by an average amount corresponding to the nugget effect. Hence, one should not expect to see a kriged contoured map that precisely matches all the observed points, but the best linear unbiased estimate of the general trend of Pu and Am in the soil environment east of 903 Pad.

1.3.2 Source of Kriging Variations in Soil-Plutonium Concentrations in Surface Soils

In constructing these spatial distribution estimates the area immediately adjacent to the 903 Pad was excluded from the kriging analysis because of extremely large variations in soil-Pu (Table 1-1). Hence, the contours of soil-Pu depicted in Figure 1-1 provided a somewhat skewed distribution of soil-Pu away from the source. Little et al. (1980) speculated that the large range in Pu concentrations in Rocky Flats Plant soils may derive from many small Pu particles agglomerated with large soil particles to form aggregates. In another polluted site, (Aiken, South Carolina) concentrations of Pu in soils especially near the source were also highly variable, with coefficients of variation usually exceeding 1.0 (Pinder and Paine, 1980). They ascribed the variations in Pu-239,240 to varying distance from point of release (75 percent), microtopographical variations (20 percent) and sampling error, which included subsampling and analytical error (5 percent).

TABLE 1-1
SOIL-PLUTONIUM CONCENTRATIONS IN SURFACE SOILS EAST OF 903 PAD

<u>Author</u>	<u>pCi/g</u>			<u>Sample Collection Method</u>
	<u>Mean</u>	<u>Standard Deviation</u>	<u>Concentration Range</u>	
Campbell (1984)	1024	978	74 - 3700	RFP
DOE (unpublished, samples taken in 1990)	267	173	2 - 566	RFP
	147	90	8 - 283	CDH

1 3 3 Ground Based Gamma Survey

Ground-based gamma survey of the area east of 903 Pad was conducted by EG&G Energy Measurements during the fall of 1990. The gamma emitting isotopes in the area east of 903 Pad were measured by High Purity Germanium Gamma Detectors (HPGe). A 150 foot grid spacing was selected to provide 100 percent land coverage. The instrument height was set at 7.2 meters above ground surface. Count time was set at 15 minutes based on the size of the area and number of measurement points needed to be accomplished in a reasonable time frame. The vehicle Mounted System, as set up, had a minimal detectable activity of 0.9 pCi/g for Am-241. These readings represent an averaged Am activity within the top 3 cm of the soil. Plutonium concentrations were derived from the linear relationship between Am and Pu in RF soils ($[Pu] = 6.23 \times [Am]$, R. Reiman, unpublished data). This estimate takes into account the original isotope mix and mixture age (EG&G-10617-1044). Kriging estimates using linear model were computed for Am and Pu distribution east of 903 Pad (Figures 1-4 through 1-7). The letters H and L in these figures represent higher and lower values than the adjacent contours. The radiological data provides an excellent spaced grid for spatial estimation of radionuclides, thus relative small error of estimates were observed near the 903 Pad (Figures 1-5 and 1-7). These small estimates resulted from an extremely large reading of Am (100 pCi/g) in one location (Figure 1-4). The results of the radiological data reinforced the notion that the spatial distribution of radionuclides near the source point can be extremely erratic.

1 3 4 Proposed Work

In order to assess the extent of Pu and Am in surficial soils within the plant boundaries, soil samples will be collected across the area identified in Figure 1-8 consisting of approximately 800 acres. Figure 1-8 was constructed on the basis of the above literature review, data analysis of unpublished material (Figures 1-1 and 1-2), and radiological surveys (Figures 1-4 through 1-7). The State of Colorado requires special techniques for construction on lands with Pu concentrations greater than 0.9 pCi/g of dry soil. To evaluate the soil-Pu values relative to this guideline, the CDH sampling protocol will be used.

The CDH sampling protocol requires 25 subsamples to be composited within a 10-acre area for Pu and Am analysis. Because of the large variations in soil-Pu near the source area, a 2.5-acre grid will be sampled immediately east of 903 Pad and around East Trenches area (Figure 1-8). This sampling design will serve two purposes: (1) increase our confidence in soil-Pu estimates around 903 Pad and East Trenches Areas, and (2) expand the number of soil data for kriging estimates. The soil sampling in the 2.5-acre area will consist of 25 subsamples for Pu and Am determination. In addition, 10-acre grid will be sampled to assess the spatial distribution of Pu and Am within the buffer zone east of 903 Pad (Figure 1-8). The soil sampling in the 10-acre area will consist of 25 subsamples for Pu and Am determination. The northwest corner of each grid will be located by survey and identified with an appropriately marked steel post. Grids will be oriented on the cardinal compass directions. The 25 subsamples for the composite sample will be located with a hand held compass and tape measure using the northwest corner as the starting point. Additional 10-acre plots will be added if large concentrations of Pu and Am would be detected north of the mound area.

1.4 VERTICAL DISTRIBUTION OF PLUTONIUM AND AMERICIUM IN SOILS EAST OF ROCKY FLATS PLANT

1.4.1 Past Work

Several studies investigated the magnitude of Pu transport down the soil column. The intensive study site which is located approximately 1.5 km east of 903 Pad was established in 1979 in response to the recommendations outlined by Seed et al (1971). Soil samples were collected between 1979 and 1983 to assess the vertical distribution of Pu in Rocky Flats Plant soils (Rockwell International, 1985). Composite samples were collected from 60-2m² plots located 1 m apart. Samples were taken from 0-5 cm and 5-20 cm intervals. The surface samples were collected using the RFP method, whereas the subsurface samples were collected using a soil auger. The mean and the standard deviation of soil-Pu concentrations in the surface and the subsurface horizons were 10.2 ± 2.7 pCi/g and 1.1 ± 0.4 pCi/g, respectively. The vertical profile of the data distribution suggests that some Pu has migrated down the soil column. Little and Whicker (1978) found that Pu concentrations in soils east of 903 Pad increased with decreased particle-size. The highest Pu

concentrations were associated with sub-micron sized soil particles for all depths (0-21 cm) Two-third of the total Pu in the soils were found in the top 5 cm The relationships between Pu concentrations and soil particle size suggests a surface-attachment mechanism of Pu to soil particles However, the absence of a consistent trend of soil-Pu with depth for the various particle sizes indicates that vertical Pu transport is not simple transport of Pu down the soil column For example, Krey et al (1978) found that 90 percent of total deposit of Pu was held in the upper 10 cm of the soil They recommended a more detailed study of soil characteristics and additional measurements of Pu concentrations with depth and time at Rocky Flats Plant

1 4 2 Proposed Work

Twenty-two soil profiles will be excavated, described and sampled in order to assess the vertical distribution of Pu-239,240 and Am-241 in soils east of the Rocky Flats Plant Ten soil profiles will be sampled in the immediate vicinity of 903 Pad, East trenches, and seep SW-53, and an additional 12 soil pits will be excavated according to soil types, direction and distance from 903 Pad The approximate location of soil pits are depicted in Figure 1-8 The soil pits will be dug in undisturbed or the least disturbed sites which are characterized by the natural short grass prairie, pasture, and valley side vegetation (Clark et al , 1980) The exact location of the soil pits will be determined in the field using air photographs, soil and topographic maps, radiological surveys and common sense Transport of soil-Pu in the soil environment is highly affected by soil type, moisture content, texture, structure and particle characteristics such as shape, density, and cohesiveness (Burley, 1990) Hence, all the major soil types east of 903 Pad will be sampled (Table 1-2) Soil pits will be excavated in all soil types east of 903 Pad for the study of vertical distribution of soil-Pu

Sampling soil profiles for radionuclides characterization is difficult for several reasons

- potential contamination of subsurface horizons during sampling from the highly contaminated surface horizons,
- collection of sufficient sample material for actinides concentrations and other soil chemical parameters, and

TABLE 1-2
SOIL TYPES EAST OF 903 PAD

Series	Family	Phase	Min-Max Slope (%)	Infiltrati on Rate	Soil Type*
Denver	Torrertic Arguistolls	clay loam	5-9	slow	27
Denver-Kutch	Torrertic Arguistolls	clay loam	5-9	slow	29
Denver-Kutch-Midway	Torrertic Arguistolls	clay loam	9-25	slow	31
Flatirons	Aridic Paleustols	sandy loam	0-3	slow	45
Haverson	Ustic Torrifluvents	loam	0-3	moderate	60
Leyden-Primen-Standley	Aridic Arguistolls	cobbly clay loam	15-50	slow	80
Midway	Ustic Torriorthents	clay loam	9-30	slow	98
Nederland	Aridic Arguistolls	sandy loam	15-50	moderate	100
Nunn	Aridic Arguistolls	clay loam	0-2	slow	102
Nunn	Aridic Arguistolls	clay loam	2-5	slow	103
Willowman-Leyden	Aridic Arguistolls	clay loam	9-30	moderate	174
Standley-Nunn	Aridic Arguistolls	gravelly clay loam	0-5	slow	149

* Soil Type number corresponds to soil type exhibited in Figure 1-8

- selecting the best sampling design to study the chemical trends in the soil profile with little or no cross contamination

In light of these difficulties special attention will be given to soil sampling from the 22 soil pits using a modified trench method (Harley, 1972) This method involves digging a trench 1.5 m long, 1.0 m wide and 1.0 m deep. One wall of the trench will be dug as a block/stair case (15 cm height each) to minimize cross contamination. The vegetation at the surface of the selected wall will be cropped closely to the surface and discarded. The soil morphology will be described according to the standard operating procedures for logging alluvial and bedrock material (SOP 3.1, EG&G 1990h). The soil will be sampled at intervals of 3 cm starting at the deepest block/stair in a given pit. Soil samples will be collected using a stainless steel scoop and template (3 cm x 20 cm) which will be pressed into the wall of the block/stair case. Three samples from each depth will be consolidated to provide a better representation of the site and to produce enough soil material for the various chemical analyses. After a sample has been collected, the soil layers below it will be cleaned to prevent possible contamination from falling soil material of the upper layer. A flag will be placed on the ground surface of a given pit and the depth below surface for each sample will be measured from the base of the flag.

1.5 PHYSIOCHEMICAL ASSOCIATION OF PLUTONIUM IN ROCKY FLATS PLANT SOILS

1.5.1 Static Soil Phase - Past Work

Sorption of Pu (IV) onto mineral surfaces, complexation with naturally occurring organic substances, and carbonate species are the dominant processes in Pu cycling in the soil environment (Polzer, 1971, Bondietti et al, 1976). Plutonium in oxidation state (IV) is very insoluble in water in the absence of complexing agents (Bondietti and Tamura, 1980). Onishi et al (1981) reviewed radionuclide adsorption/desorption mechanisms in soils and concluded that strong adsorption of Pu occurs over the pH range of 4 to 8 and is easily complexed with humic acids, oxalate, and acetate ions. Bondietti et al (1976) removed 82 percent of the soil-Pu by repeated bleaching experiment with NaOCl at pH 9.5, which minimized inorganic mineral

destruction (Lavkulch and Wiens, 1970), and thus would not extract occluded Pu in sesquioxides. This removal suggests that a large portion of soil-Pu is associated with organic carbon (C), and that Pu is associated with the soil via surface-sorbed mechanisms. The release of organic chelates agents is strongly dependent on pH and decalcification processes within the soil (Bondietti and Tamura, 1980).

Phase I RI found occasional elevated concentrations of Pu (> 0.05 pCi/l) in seep waters (SW-50, SW-53, and SW-54) (Rockwell International, 1987a). Although the total concentration of Pu in the soil matrix is important information in appraising the potential hazard, total concentrations do not provide sufficient data to assess potential transport and availability of Pu in the soil environment. Hence, in order to better understand the mechanisms of transport of Pu in soils and seep waters, a sequential extraction of soil from five soil profiles above seep SW-53 (locations X1 to X5 in Figure 1-8) will be conducted. Soil samples will be collected at 3-5 cm intervals. The procedure for sampling the soil profiles is described above. This study, in conjunction with the soil interstitial waters investigation (Mobile Soil Phase, see below), will provide the necessary information to appraise the nature of Pu transport in the soils of Rocky Flats.

1.5.2 Static Soil Phase - Sequential Extraction Experiments

Use of total Pu concentrations as a criterion to assess the potential effects of soil contamination implies that all forms of Pu have an equal impact on the environment. It is clear that such an assumption is untenable. Conceptually, the soil can be partitioned into specific fractions which can be extracted selectively by using appropriate extractants (Tessier et al., 1979). Sequential multiple dissolution techniques which selectively extract soil material with resulting release of its associated metals have been extensively used in soil science and geochemical exploration (Chao, 1984). The purpose of the selective sequential extraction in the proposed study is to elucidate the mode of occurrence and possible transport of Pu and Am in soils. It should be noted, however, that the partitioning of Pu and Am obtained by this procedure is operationally defined, as it is influenced by experimental factors such as the choice of reagents, the time of extraction, and the ratio of extractant to soil (Tessier et al., 1979). In addition, inherent analytical problems such as incomplete selectivity and readsorption may seriously affect the extracted metal concentrations. For example, Rendell et al. (1980)

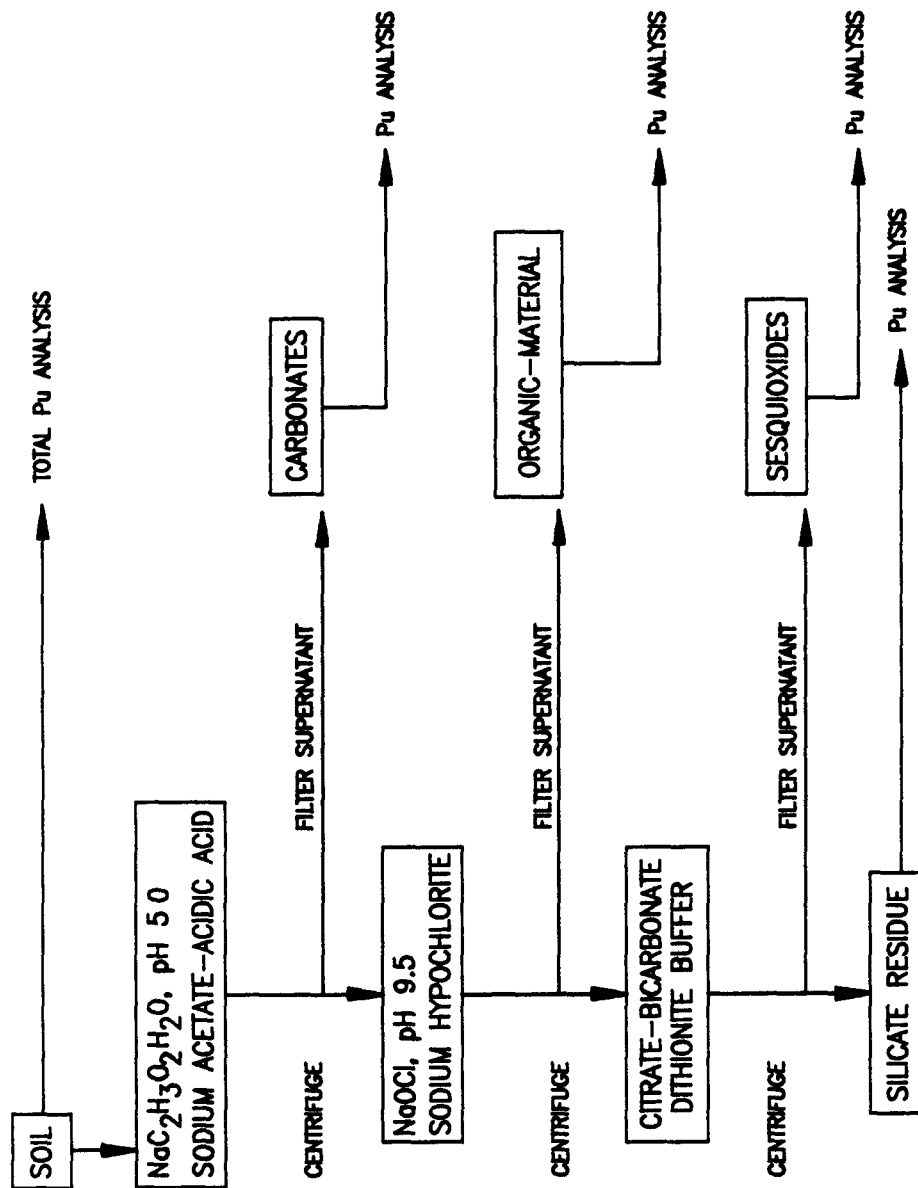
found that added cadmium (Cd), lead (Pb) and copper (Cu) were readsorbed by uncontaminated river sediments during over-night extraction with selected extractant solutions Gruebel et al (1988) showed that arsenic (As), and selenium (Se), associated with freshly precipitated amorphous iron oxides were readsorbed onto other minerals unaffected by the reductive extractant Kheboin and Bauer (1987) doped traced metals into humic acid (Cu), iron sulfides, zinc (Zn), calcite (Pb), and iron hydroxides [Cu, nickel (Ni)] but failed to recover these metals in the appropriate fraction using the selective procedure outlined by Tessier et al (1979) These findings imply that selective extraction may not be suitable for distinguishing the phase-association of metals in soils Belzile et al (1989) have challenged the above results and asserted that postextraction readsorption of metals occurred due to improper experimental conditions of the sequential extraction and mineral phases They quite convincingly showed that trace elements spikes (< 100 percent of the amount present in the control samples) were recovered within the limits given by the experimental errors ± 10 percent

1 5 3 Static Soil Phase - Proposed Work

Plutonium determination will be performed on four sequential selective extracts in triplicates to assess the physicochemical association of Pu with calcium carbonate (CaCO_3), organic C, sesquioxides, and residue (Figure 1-9) In this study, we shall use the gamma emitter isotope Pu-237 as a tracer to assess the degree of postextraction readsorption of Pu isotopes (Pu-239,240) during the various extractions performed on the soils In addition, the sequence of extractions shown in Figure 1-9 will be modified to test the uniqueness of individual extraction

1 5 3 1 Tracer Study

Spikes of Pu-237 will be added to soil samples (triplicates) before each extract step (Figure 1-9) The percentage of spike recovery and possible readsorption of the tracer will be carefully determined In case of serious postextraction readsorption (> 15 percent) the selective sequential extraction will not be performed In case the selective sequential extraction procedure is rejected, samples collected from pits X1 to X5 will only be analyzed for total Pu



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SEQUENTIAL EXTRACTION FOR SOIL-Pu

FIGURE 1-9

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1 5 3 2 Partitioning of Soil Phases

Fraction 1 Carbonates. In the soil environment, carbonates are susceptible to changes in pH which will induce the release of adsorbed Pu. Carbonates will be removed by 0.5 molar (M) sodium acetate-acetic acid buffer solution ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{H}_2\text{O}$), adjusted to pH 5. This buffer treatment removes metals held in carbonates (coprecipitate with carbonates and/or adsorbed by iron and manganese oxides which have precipitated onto the carbonates) (Jenne, 1977). This buffer apparently does not attack the resistant sesquioxides phases to any great extent and leaves the lattice structure of silicate minerals intact (Chao, 1984).

Fraction 2 Organic. In natural conditions, organic carbon is gradually decomposed which may lead to release of soluble and colloidal Pu. The organic C will be extracted by NaOCl at pH 9.5. Lavkulich and Wiens (1970) removed up to 98 percent of the oxidizable organic carbon from 16 soil samples by three successive extractions with sodium hypochlorite. The sodium hypochlorite treatment is the preferable solution for extracting Pu from soil organic matter because it does not appear to dissolve sesquioxide phases. It should be noted, however, that sodium hypochlorite will attack sulfides that may present in the sample.

Fraction 3 Sesquioxides. Sesquioxides are excellent scavengers of trace metals and are extremely unstable under anoxic conditions. There are various techniques to extract iron, manganese, and aluminum oxides in soils. These methods were developed to selectively dissolve the various mineralogical forms and degree of fineness of the sesquioxides present in soils. In the context of the proposed study, the citrate-bicarbonate-dithionite buffer method (Jackson et al., 1986) is superior to other methods because it dissolves amorphous sesquioxides completely whereas the highly crystalline sesquioxides (e.g., hematite and goethite) will be partially dissolved. The degree of dissolution of the highly crystalline sesquioxides is dependent on the crystallinity and the fineness of grinding of the oxides. Hence, in order to obtain complete dissolution of crystalline sesquioxides, the soil samples will be finely ground and three multiple extractions will be performed.

Fraction 4 Residue. After removal of the above chemical phases from the soil sample, the residue consists of silicates and some other resistant mineral species such as ilmenite and magnetite. The residue will be dissolved by strong digestion with hydrofluoric acid in conjunction with nitric acid.

1.5.3.3 Experimental Conditions

- (a) **Bound to Carbonates** The soils will be extracted for 5 hours with 20 milliliters (ml) of 1M sodium acetate-acidic acid solution adjusted to pH 5.0. Detailed description of this extraction is given by Nelson (1982).
- (b) **Bound to Organic** The residue from (a) will be extracted for 5 hours with 20 ml of 1M sodium hypochlorite solution adjusted to pH 9.5. Detailed description of this extraction is given by Hoffman and Fletcher (1981).
- (c) **Bound to sesquioxides** The residue from (b) will be extracted for 6 hours with 100 ml of 0.3M sodium citrate mixed with 1M sodium carbonate solution and appropriate amounts of sodium dithionite and sodium chloride salts. This extract will be repeated three times to assure almost complete dissolution of highly crystalline iron oxides. Detailed description of the extraction is given by Jackson et al. (1986).
- (d) **Residual** The residue from (c) will be digested by a 5:1 mixture of hydrofluoric and perchloric acids. For a 1-gram (g) (dry weight) sample, the soil will be first digested in a platinum crucible with a solution of concentrated HClO_4 (2ml) and HF (10ml) to near dryness. Subsequently, a second addition of HClO_4 (1ml) and HF (10ml) will be made, and again the mixture will be brought to near dryness. Finally, HClO_4 (1ml) will be added and the sample will be evaporated until the appearance of white fumes. Further details of this extraction is given by Lim and Jackson (1982).

After each extraction the sample will be centrifuged at 10,000 rpm for 30 minutes. The supernatant will be removed with a pipet and prepared for Pu analysis. The residue will be washed with 10 ml of deionized water to remove residual salt from the previous extraction. The volume of the rinse water will be kept at a minimum to avoid excessive solubilization of organic matter.

In addition, the following analyses will be conducted on all samples from the five soil profiles (locations X1 to X5, Figure 1-8) upslope from SW-53: (1) soil organic C, (2) soil pH, (3) CaCO_3 content, (4) sesquioxides content, and (5) specific conductance. The specific conductance will be used to estimate the ionic strength of the soil slurry (Lindsay, 1979).

1.5.4 Mobil Soil Phase - Past Work

Reports of Pu and Am movement in ground water over distances beyond several meters are rare. Hakonson et al (1981) reviewed the transport of Pu in terrestrial systems and asserted that vertical leaching of soluble Pu through the soil is a potentially important phenomenon. Onishi et al (1981) concluded that adsorbed Pu can be readily moved through the aqueous environment in colloidal form. Recently, Penrose et al (1990) found that Pu and Am were transported in ground water for at least 3390 meters downgradient from the point of discharge. Plutonium and Am were tightly or irreversibly bound to colloidal material (25 to 450 nm). Krey et al (1978) attributed the successful application of the diffusion term in their soil-Pu transport model, at several diverse sites east of 903 Pad, to transportability of Pu in soil interstitial waters and not to soil characteristics.

Little research has been conducted on the transport of actinides within the soils and to seeps and streams at the Rocky Flats Plant. Moreover, there are no studies on the physicochemical characteristics of interstitial waters in soils and sediments from Individual Hazardous Substances Sites (IHSSs) on plant-site. The excavation of 30 soil pits will allow for the installation of automated soil solution samplers in order to measure and characterize the movement of water and radionuclides down the soil column. More specifically, soil

solution samplers will be installed in the soils above seeps SW-50, SW-53, and SW-54 to study the movement of both water and radionuclides (colloidal and dissolved) down the soil column and to the seeps downslope

1 5 5 Mobile Soil Phase - Proposed Work

Environmental fate of actinides in soils are usually studied by extracting the soil matter. In general, these analyses fail to provide important information regarding the transport mechanisms of pollutants within the soil column. Hydrological analysis of the frequency, duration and intensity of summer precipitation events and spring snowmelt events, coupled with direct measurements of solute transport in soils will provide essential information to assess the form and magnitude of actinide movement in soil.

The proposed research design is based on three hypotheses

- leaching episodes in the soils will transport solute and colloidally-bound actinides down the soil column,
- freely flowing waters in the soil environment will carry different actinide concentrations than soil solutions collected at higher matrix potentials, and
- the occasional elevated concentrations of Pu in seep SW-53 were originated by vertical leaching of Pu from the soil environment upslope

Testing these hypotheses will require in-situ sampling of soil interstitial waters over time. More specifically, it will be necessary to develop a fully-automated, remote-controlled soil solution sampling system that is capable of (a) collecting freely flowing water [0-5 kilo Pascals (kPa) matrix potential] mainly via macropores, (b) collecting soil solutions flowing in micropores at higher matrix potential (5-40 kPa), and (c) provide accurate and timely measurements of incoming precipitation. This apparatus will consist of five major modules: an automated zero-tension sampler, in which freely flowing water mainly in macropores (formed by frost heave cycles and swelling and shrinking of clays), will be accurately collected for assessing the subsurface flow during and after major precipitation events, a fluxmeter which will provide the unsaturated flux as the soil dries out as well as soil solutions for radiochemistry analyses, tipping bucket rain gauge, time

domain reflectometry (TDR) soil moisture probes which will measure in-situ soil water content, and telemetry communication which will send the data collected in the field to a base station at T130B (Figure 1-10)

The objectives of the proposed work are to

- estimate the importance of vertical flow in the soil environment upslope from seep SW-53 during and after major precipitation events, and
- assess the relationships between soil-Pu in the interstitial waters and Pu in the seep SW-53

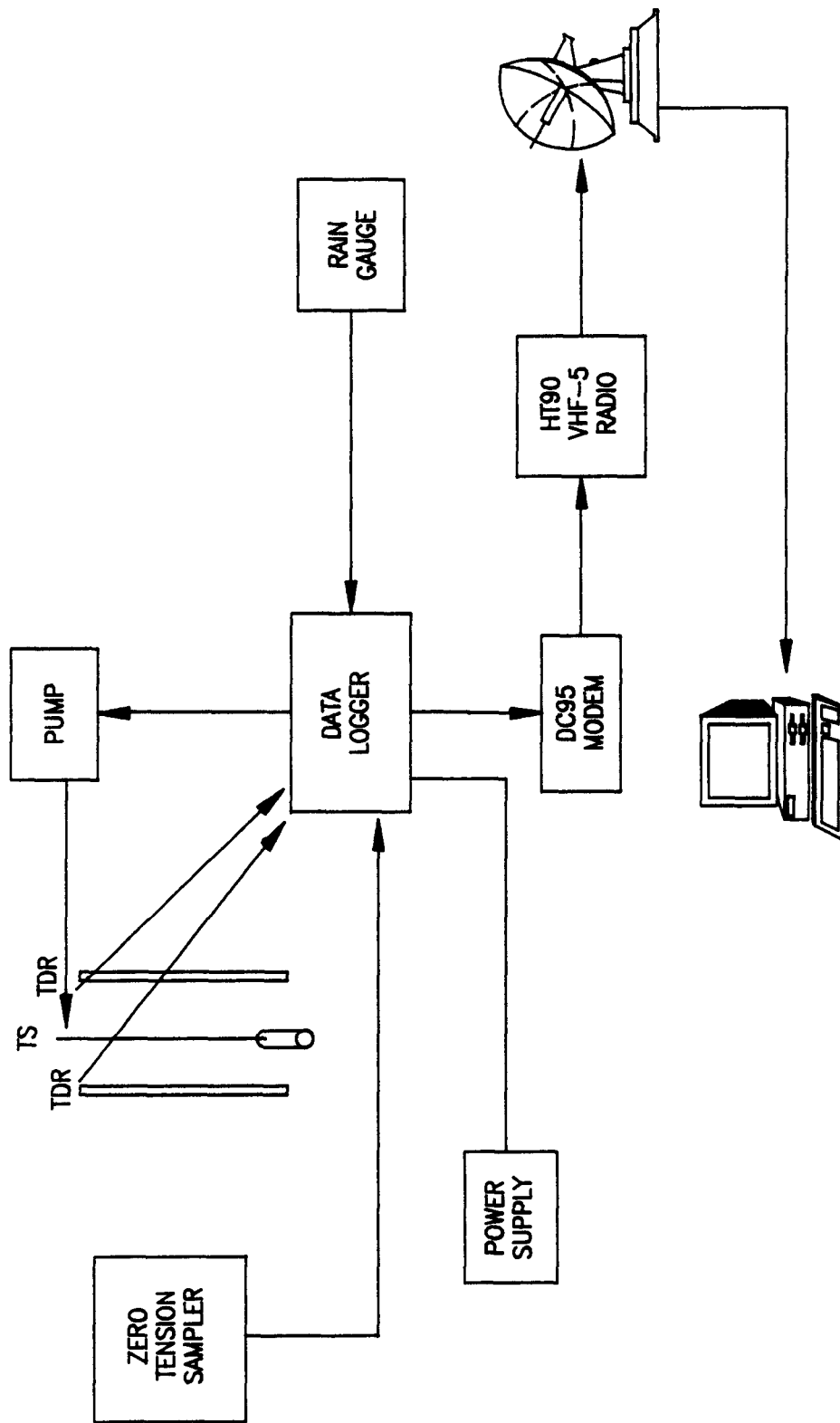
The water flow data obtained in-situ will be used to test the infiltration rates and flow estimates calculated by the unsaturated flow model developed by Colorado State University (CSU) (mid-1991) for the area east of 903 Pad. The chemical characterization study will include (1) total concentrations of Pu and Am in soil interstitial waters that move freely (0-5 kPa) down the soil column and (2) fractionation of actinides in colloidal and dissolved ($< 0.1 \mu\text{m}$) phases in freely flowing waters (0 - 5 kPa) and various matrix potentials (5 - 10, 10 - 30, 30 - 50 kPa)

1.5.5.1 Soil Solution Samplers

The chemical characterization will be performed using the soil solution sampler equipment described in the following sections. These samplers will include zero-tension samplers and flex meters.

Zero-tension sampler

The zero-tension sampler will be made of 40-cm segments of plexiglass (25 cm width) with one end plugged with a plexiglass stopper containing a collecting tube and the other end sharpened. The sharpened end will be driven into the pit face with a mallet to ensure minimal structure and textural disturbance to the soil. The water sampled by the zero-tension sampler will be collected by a 2-liter bottle mounted on a load cell. The temperature of the soil interstitial waters and the soil matrix will be measured by a temperature probe. The temperature and amount of water in the collection bottle will be simultaneously transmitted to a data logger.



TDR = TIME DOMAIN REFLECTOMETRY
 TS = TEFLON CYLINDER TENSION SAMPLER

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SOIL SOLUTION SAMPLER APPARATUS

FIGURE 1-10

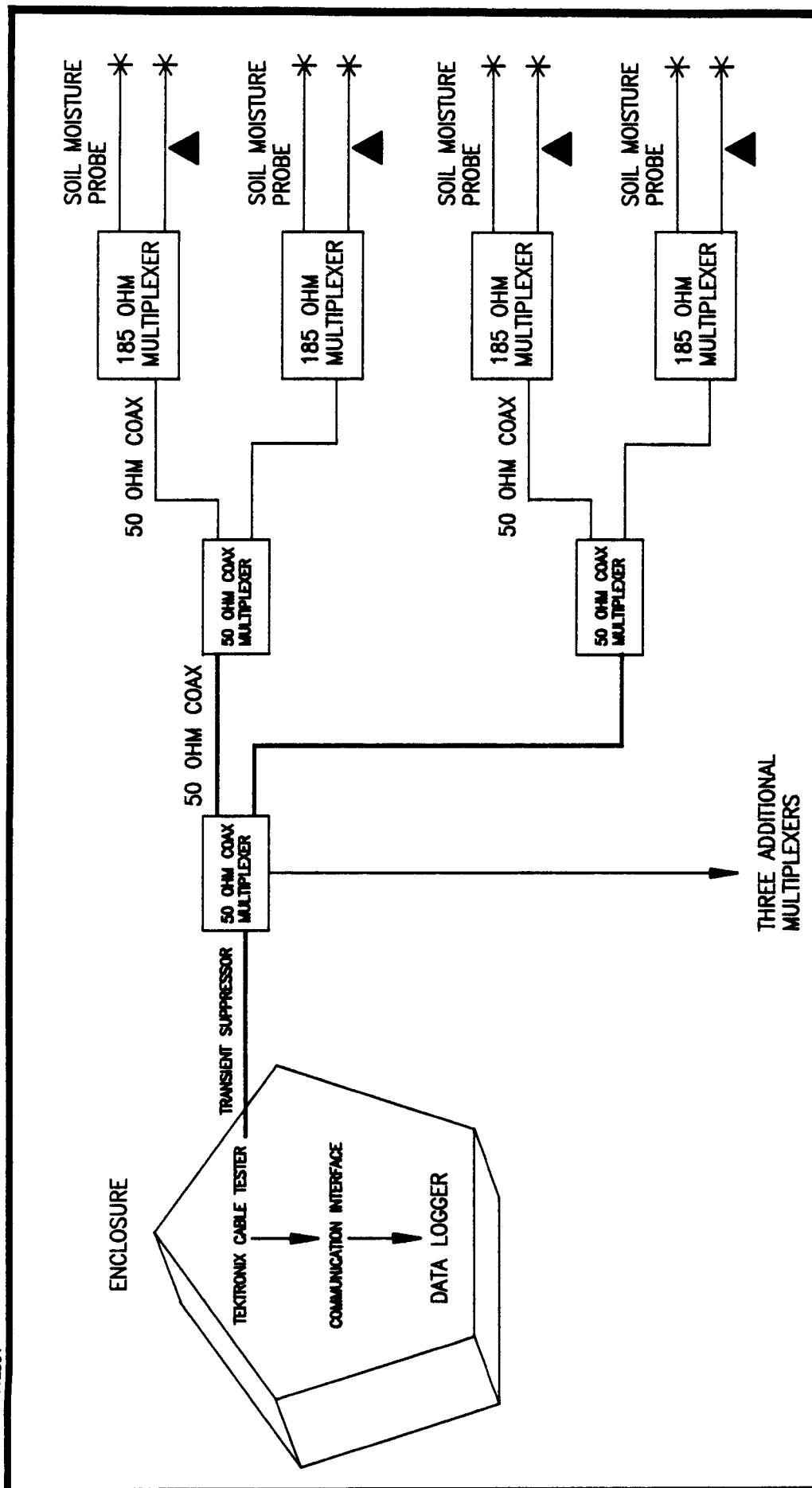
February, 1991

The transmitted information will be transferred daily to the base station via telemetry. Sending the data via telemetry to the base station (T130B) will provide crucial information regarding the time and frequency of field sampling.

The soil pits will be refilled after access tubes are inserted to prevent convergence flow and to minimize further disturbance. The zero-tension soil solution samplers will be installed upslope of seep SW-53 every 10-15 cm down the soil column to the depth of the caliche horizon or other semi-impermeable layer in the five soil pits.

Fluxmeter

The fluxmeter consists of three components: a Teflon cylinder soil water sampler which is treated with silica to reduce hydrophobicity, three TDR soil moisture probes, and a portable vacuum pump with a buffer container. Each Teflon sampler will be installed with three TDR soil moisture probes around it and connected, via Teflon tubing, to 2-liter collecting bottles equipped with a special screw cap of polyethylene with teflon gasket and fittings. The 2-liter collecting bottles will be residing inside a thermo-box which will minimize temperature fluctuations in the field. Two types of Teflon cylinder soil water samplers will be used: Teflon cylinder with average pore size of 10 μm for sampling large water volumes during short flow episodes, and Teflon cylinder with average pore size of 5 μm for normal operational conditions. Ten Teflon cylinder soil water samplers will be installed at five different depths in each pit excavated for the zero-tension sampler. The Teflon cylinder soil water samplers will be installed into the face of the soil pit using stainless-steel rod. The soil moisture probes will be connected via coaxial cable to a Tektronix cable tester, equipped with a communication interface, to a datalogger (Figure 1-11). Once the soil moisture of the soil exceeds a pre-set value the vacuum pump will be activated to produce an equivalent vacuum inside the tension sampler. The equivalent vacuum will be derived from the linear relationships between soil moisture and matrix potential values in the range of 0.1 to 50 kPa.



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SCHEMATIC DIAGRAM OF
 TDR SOIL MOISTURE PROBES

FIGURE 1-11

February, 1991

The soil interstitial waters collected by the zero-tension samplers and the tension samplers will be filtered on the day of sampling using 0.45- and 0.1- μ m Millipore filters. The total colloidal bound Pu will be determined from the material that was retained on the filters. The dissolved Pu will be determined from the water that passed through the filter.

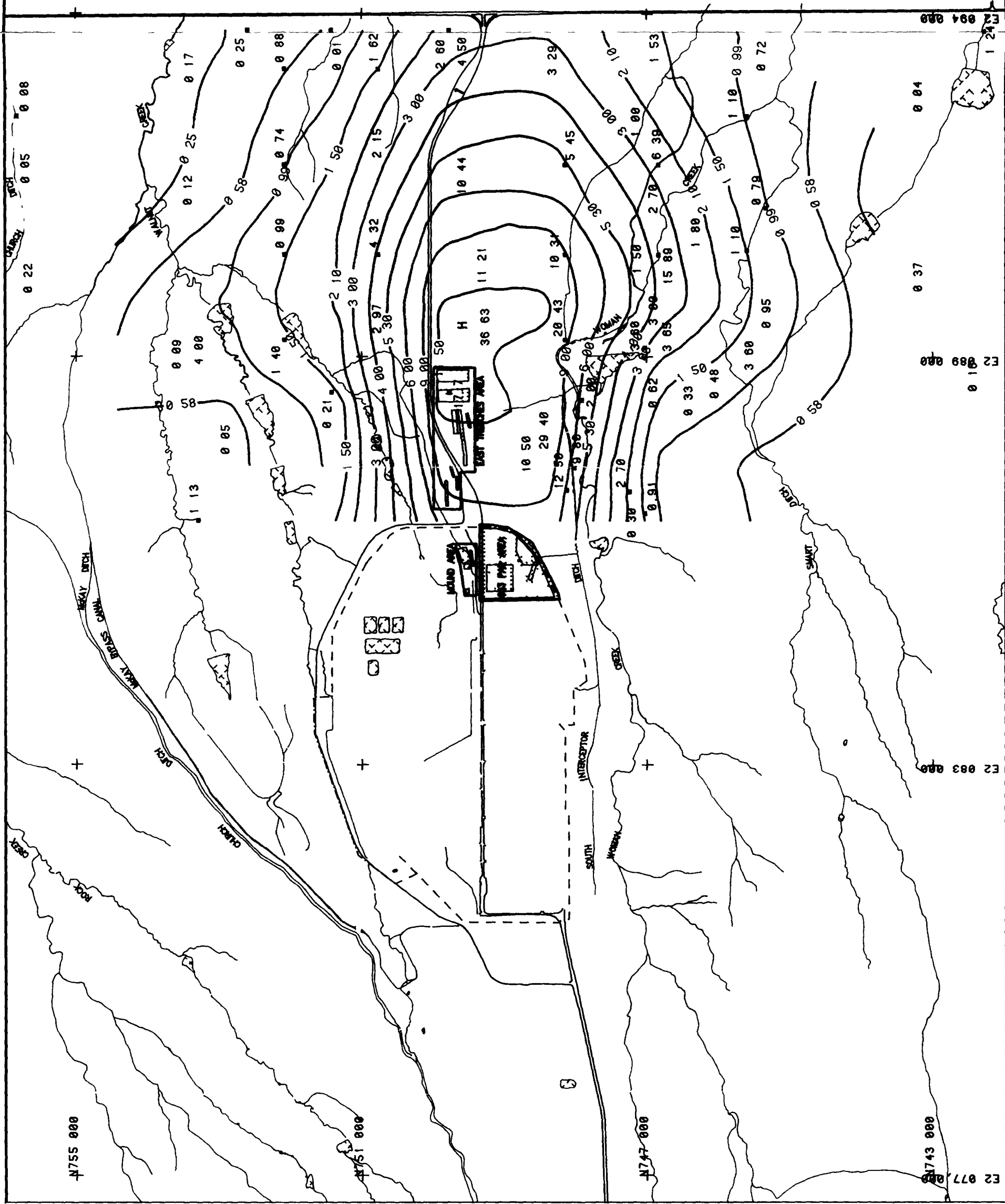
1.5.5.2 Precipitation Events Simulation

The frequency, duration and intensity of summer precipitation will be determined by a tipping bucket rain gauge. This rain gauge is an integral part of the proposed apparatus and will be mounted in the middle of the transect. The rain gauge will simultaneously transfer the data to the data logger which will transmit this information via telemetry to the base station in T130B. The amount and nature of precipitation and soil water flux will be recorded and checked daily. The frequency of field sampling will be determined on the basis of the transmitted data. This data will be used to prepare a precipitation model for hydrologic simulation and analysis.

The amount of water that can be collected by this apparatus in Rocky Flats Plant soils is currently unknown. One to two liters of interstitial waters were collected every week during snowmelt and after every major precipitation event in forested and alpine ecosystems using a simplified version of the proposed apparatus (Litaor, 1988). Hence, two rain simulation experiments will be conducted before the beginning of the precipitation season. The first experiment will be used to verify that all the components of the apparatus are interfacing and communicating with each other and the base station. Calibration of the load cells and the TDR soil moisture probes will be performed during the first rain simulation experiment. The magnitude and duration of the second simulated rain will be determined by reviewing precipitation data collected at Rocky Flats Plant in the last five years. Soil solution collected during the second simulation experiment will be submitted for radionuclides analyses.

The importance of hydrologic model simulation of rain and snow precipitation in the proposed work can be summarized as follows: (1) rain simulation yields more rapid results, especially where the testing of the

extreme conditions (e g , rainfall in arid and semi-arid conditions), and (2) rain simulation is more controlled inasmuch as one can take appropriate measurements with selected intensities and durations The rain simulator described by Ghodrati et al (1990) will be used in the proposed work This rain simulator can employ spatially uniform application of water to small plots (1-2 m²) The simulated rainwater will have the same ionic strength as averaged rainwater observed at Rocky Flats Plant



EXPLANATION

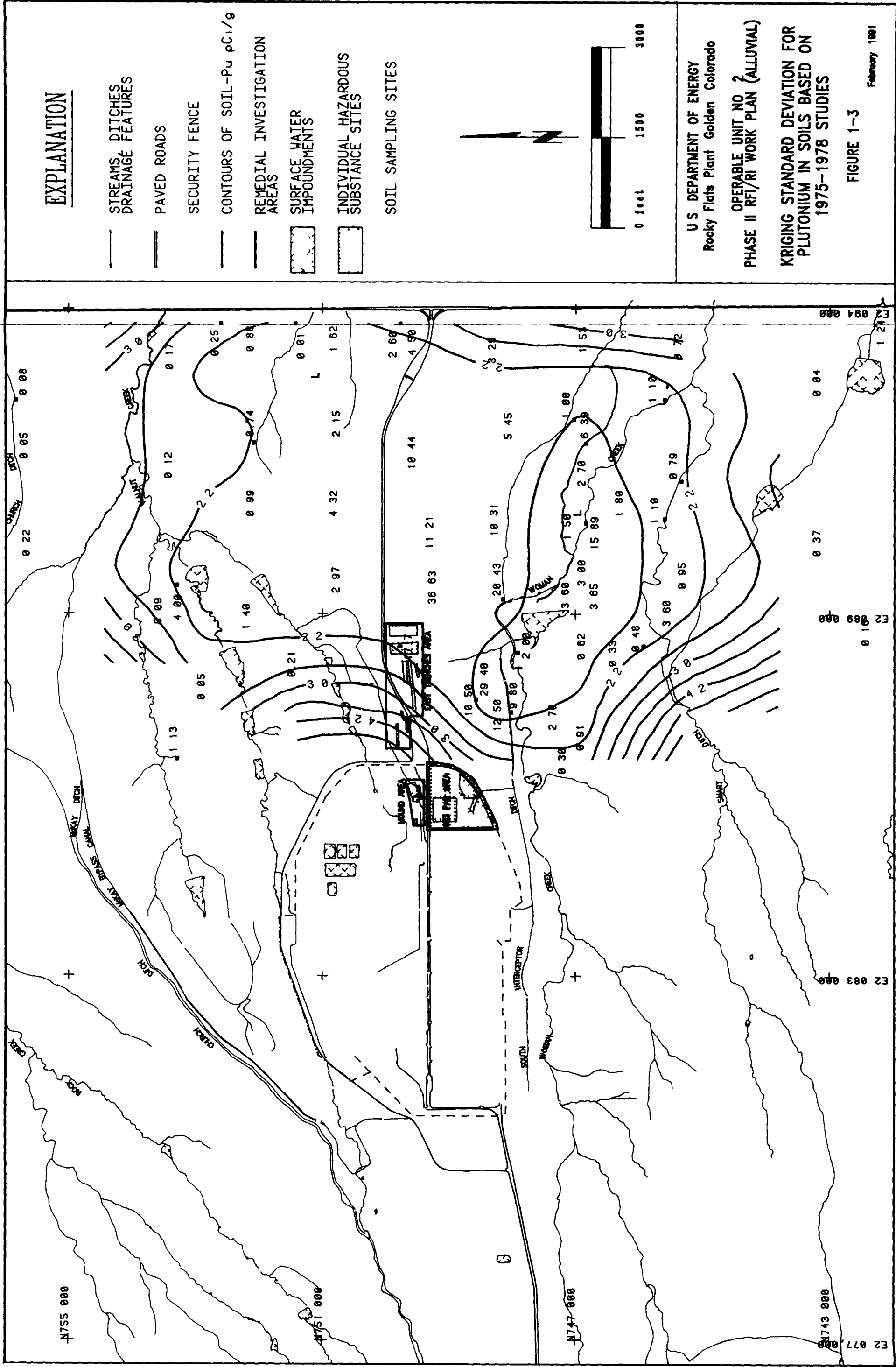
- STREAMS, DITCHES, DRAINAGE FEATURES
- PAVED ROADS
- SECURITY FENCE
- CONTOURS OF SOIL-Pu pCi/g
- REMEDIAL INVESTIGATION AREAS
- SURFACE WATER IMPOUNDMENTS
- INDIVIDUAL HAZARDOUS SUBSTANCE SITES
- SOIL SAMPLING SITES



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KRIGING ESTIMATES FOR
PLUTONIUM IN SOILS BASED ON
1975-1978 STUDIES

FIGURE 1-1
February 1981



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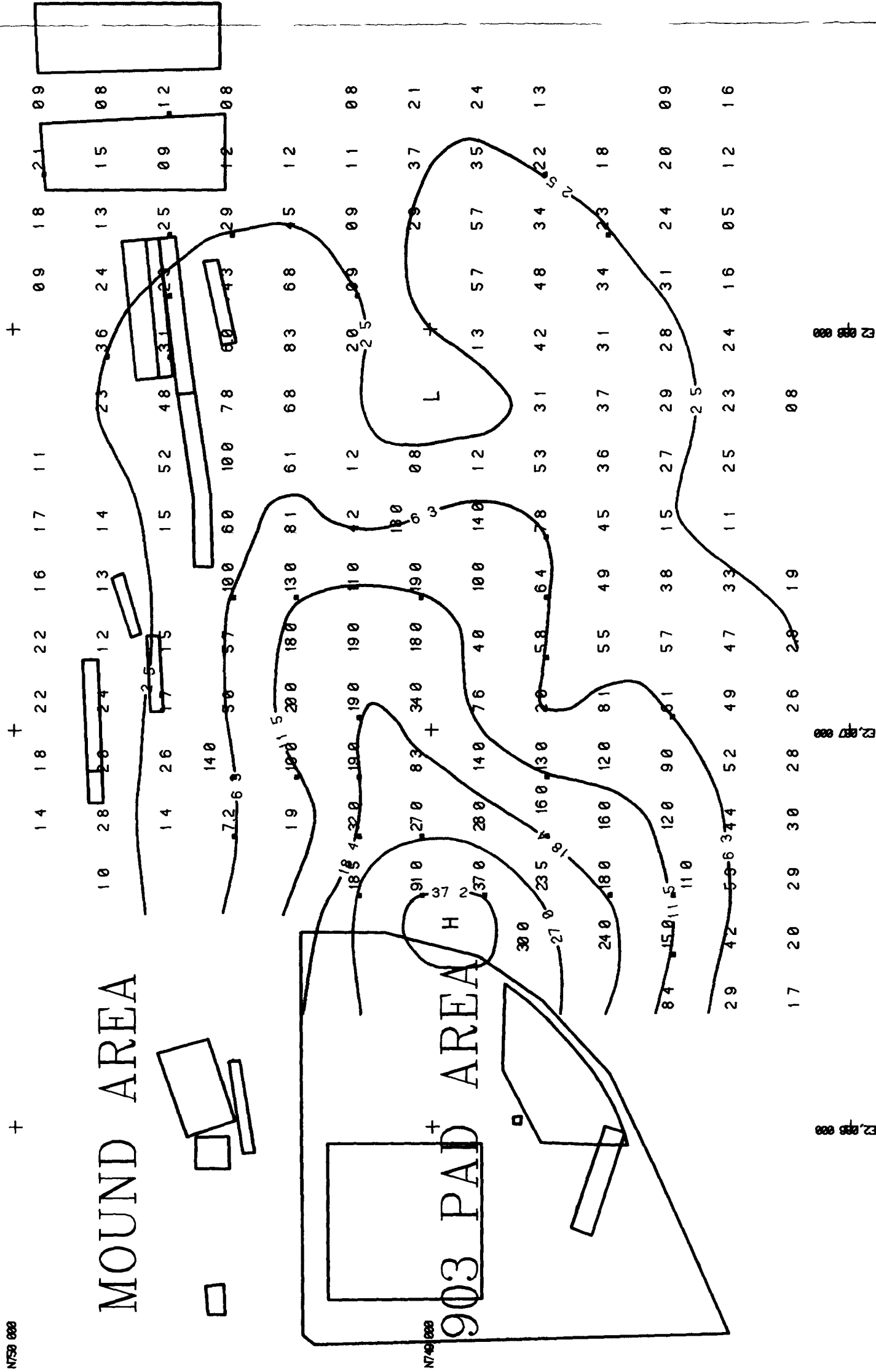
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KRIGING STANDARD DEVIATION FOR
PLUTONIUM IN SOILS BASED ON
1975-1978 STUDIES

FIGURE 1-3
February 1981

Note Amer c um concentrations
were der ved from
radiological survey 1989

EAST TRENCHES AREA



EXPLANATION

INDIVIDUAL HAZARDOUS
SUBSTANCE SITES

CONTOURS OF SOIL-Am pCi/g

SOIL SAMPLING SITES



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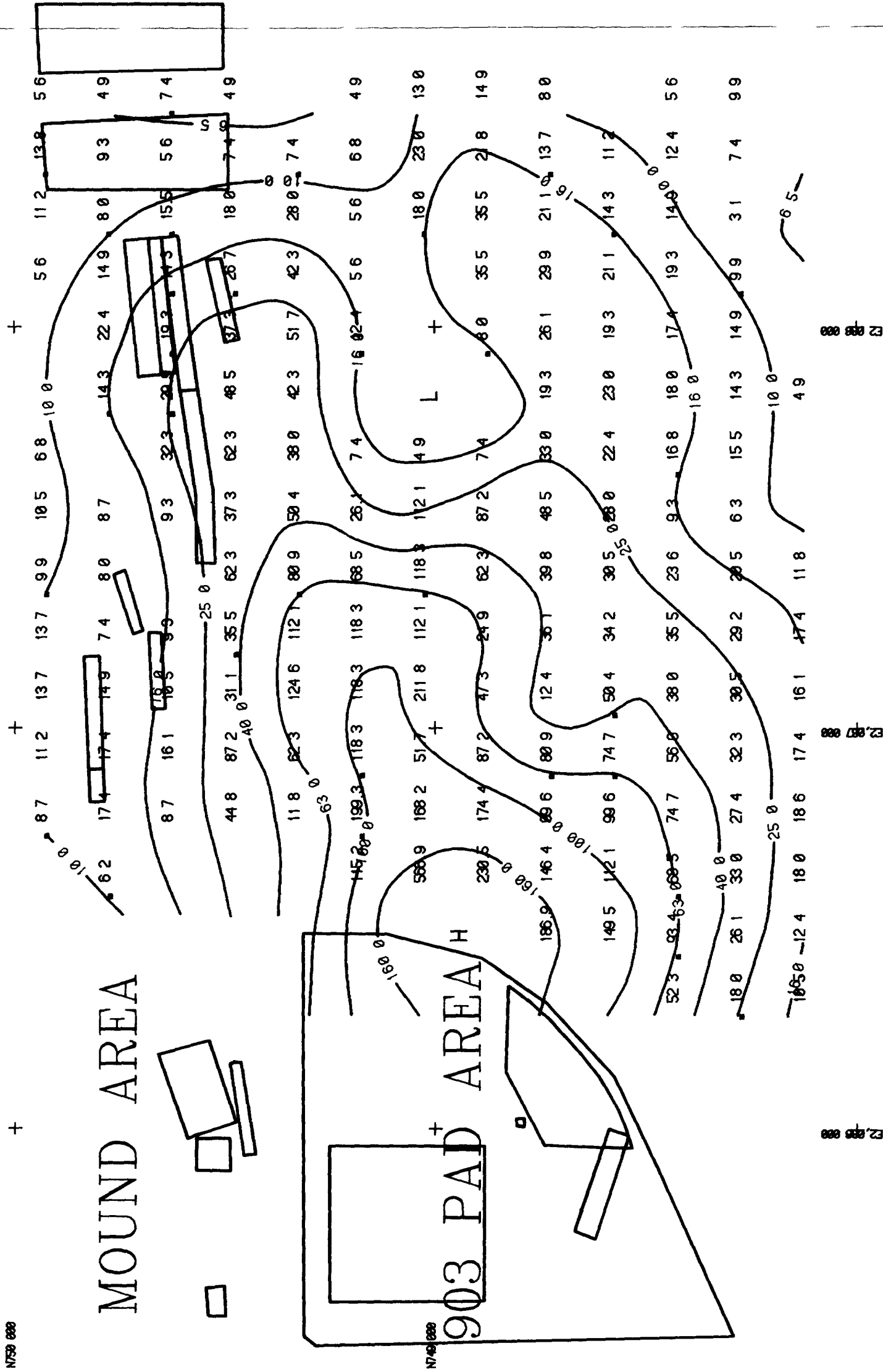
KRIGING ESTIMATES FOR
AMERICIUM IN SOILS
BASED ON 1990 STUDIES

FIGURE 1-4

February 1991

Note Plutonium concentrations were derived from Americium concentrations which in turn were derived from radiological survey 1989

EAST TRENCHES AREA



EXPLANATION

— INDIVIDUAL HAZARDOUS SUBSTANCE SITES

— CONTOURS OF SOIL-Pu pCi/g

— SOIL SAMPLING SITES

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KRIGING ESTIMATES FOR
PLUTONIUM IN SOILS
BASED ON 1990 STUDIES

FIGURE 1-6

February 1991

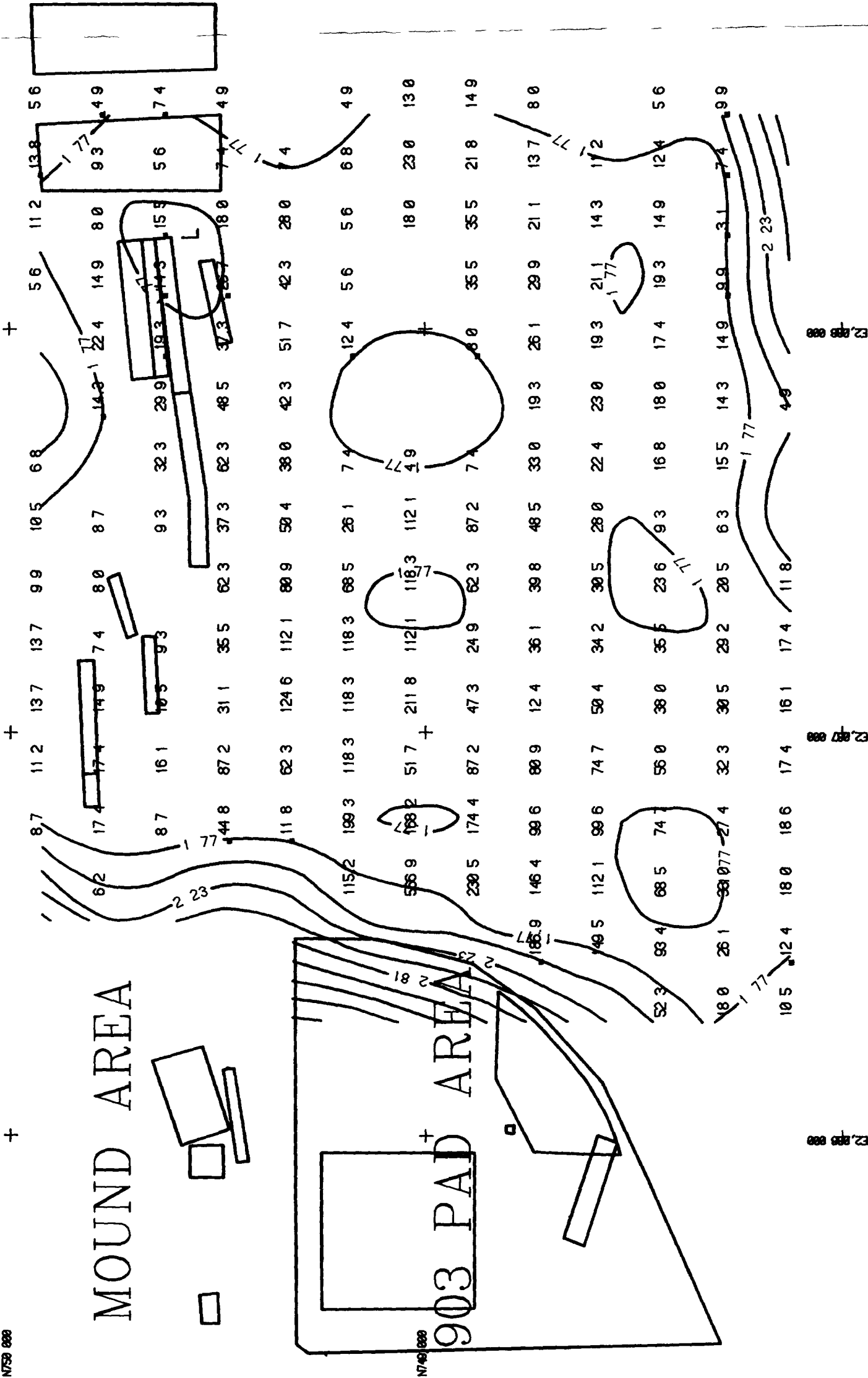
EXPLANATION

INDIVIDUAL HAZARDOUS
SUBSTANCE SITES

CONTOURS OF SOIL-Pu pCi/g

SOIL SAMPLING SITES

EAST TRENCHES AREA



EXPLANATION

ESTIMATED MAXIMUM EXTENT OF
SURFICIAL SOILS CONTAINING
TWO dpm/g ACTIVITY BY
CDH PROTOCOL



10 ACRE SAMPLING
PLOT LOCATIONS



2 5 ACRE SAMPLING
PLOT LOCATIONS



SOIL PROFILE SAMPLING
LOCATIONS FOR
OPERABLE UNIT 2



SOIL TYPES



LOCATION OF SOIL
X₁ to X₅ SOLUTION SAMPLERS



0 feet 1000 2000

CONTOUR INTERVAL 20 FEET

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PROPOSED SURFICIAL SOIL
SAMPLING LOCATIONS

FIGURE 1-8

February, 1991

